



Formation of benzo[*ghi*]fluoranthenes by palladium catalyzed intramolecular coupling

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Abstract

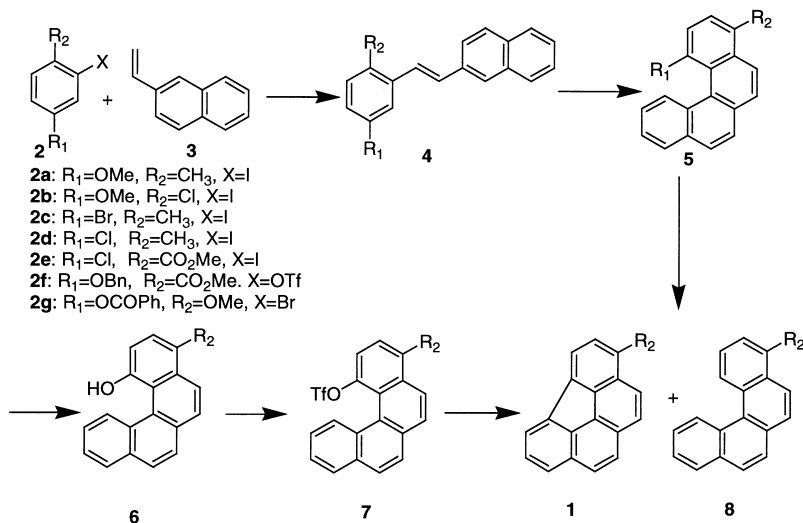
A novel synthesis of benzo[*ghi*]fluoranthenes by palladium mediated coupling is reported. The high yields, mild reaction conditions and functional group tolerance are an advantage of this method. © 2000 Elsevier Science Ltd. All rights reserved.

Stimulated by interest in fullerenes, the synthesis of polycyclic aromatic hydrocarbons (PAHs) has become an active field. Benzo[*ghi*]fluoranthene, **1**, a sub-unit of C₆₀ has been synthesized in low yield by dehydrogenation of benzo[*c*]phenanthrene,¹ and by flash vacuum pyrolysis of appropriate precursors.^{2,3} The major drawback of FVP is low to modest yield, the small scale involved, and the minimum functional group tolerance. Since intramolecular palladium mediated coupling of bromides or iodides with aromatic rings has been reported,⁴ palladium chemistry with its mild reaction conditions and wide functional group compatibility is an attractive route to PAHs. Rice and Cai have reported the synthesis of several fluoranthenes and benzofluoranthenes by a palladium catalyzed intramolecular arene–triflate coupling.⁵ We now report an efficient synthesis of benzo[*ghi*]fluoranthenes by palladium mediated intramolecular coupling employing bromides, triflates, and chlorides as leaving groups (Scheme 1).

trans-Stilbenes, **4**, were prepared by the Heck reaction from **2** and **3** in yields of 66 to 88% using [1,1'-bis(diphenylphosphino)ferrocene]palladium(II) chloride:CH₂Cl₂ (1:1) [Pd(dppf)Cl₂] as catalyst. Although the bromide **2g** with an *o*-methoxy was much less reactive with this catalyst, the use of *trans*-di- μ -acetatobis[2-di-*o*-tolylphosphino)benzyl]dipalladium(II) [palladacycles]⁶ with higher boiling tributylamine in DMA gave **4g** in 71% yield. (Table 1)

Table 2 illustrates the photolysis of **4** to **5** in the presence of propylene oxide and iodine in Pyrex.⁷ Although most functional groups were tolerated in the photolysis reaction, when both of OCOPh and OMe were present in **4g**, the photolysis gave complex products possibly from the debenzoylation–oxidation during the photolysis.⁸ However, using benzoxy rather than benzoate as the protecting group gave **5g** in 89% yield.

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Scheme 1.

Table 1

Formation of stilbenes by the Heck reaction

Reactants	Products	Conditions	Yields (isolated, %)
2a	4a	a	88
2b	4b	a	76
2c	4c	a	77
2d	4d	a	81
2e	4e	a	66
2f	4f	a	70
2g	4g	b	71

^aPd(dppf)Cl₂ (5%), DMF, Et₃N, 100°C, 20 h. ^bPalladacycles (5%), Bu₃N, DMA, 140°C, 20 h.

Table 2

Formation of benzo[*c*]fluoroanthrenes by photolysis

Reactants	Products	Yields (isolated, %)
4a	5a	90
4b	5b	99
4c	5c	56
4d	5d	77
4e	5e	89
4f	5f	95
4g^a	5g^a	89

^aR₁ is OBn.

Triflates, **7**, were obtained in excellent yield either by standard demethylation of OMe (**5a** and **5b**) or debenzylation of OBn (**5f** and **5g**) followed by treatment with triflic anhydride.

Table 3 shows that the treatment of triflate or bromo benzo[*g*]phenanthrenes with bis(triphenylphosphine)palladium(II) chloride [Pd(PPh₃)₂Cl₂] in DMF or DMA gives **1** in excellent yield.⁹ Contrary to previous reports in which one or more equiv. of PPh₃ was needed to achieve satisfactory yields in the presence of electron-donating substituents,^{5,10} the formation of **1g** proceeded well without additional PPh₃.

Table 4 demonstrates the formation of benzo[*ghi*]fluoroanthrenes from chloro benzo[*g*]phenanthrenes. When an electron-donating methyl group was *para* to chlorine, neither Pd(PPh₃)₂Cl₂ nor palladacycles

Table 3
Palladium catalyzed intramolecular couplings from triflates and the bromide

Reactants	Products	Conditions	Yields (isolated, %)
7a	1a	a	92
7b	1b	a	88
5c	1a	b	85
7f	1f	a	93
7g	1g	a	94

^aPd(PPh₃)₂Cl₂ (5-10%), DMF, DBU, LiCl, 140°C, 6h. ^bPd(PPh₃)₂Cl₂ (5%), DMA, NaOAc, 140°C, 6 h.

Table 4
Palladium catalyzed intramolecular couplings from chlorides

Reactants	^a Products	Conditions	Yields (isolated, %)
5d	5d:1d (100:0)	b	80
	5d:1d (80:20)	c	
	5d:1d (10:90)	d	
	5d:1d (50:50)	e	
5e	5e:1e:8e (30:40:30)	b	79
	5e:1e:8e (28:45:27)	f	
	5e:1e:8e (0:100:0)	g	

^aProduct ratios determined by ¹H-NMR. ^bPd(PPh₃)₂Cl₂ (10%), NaOAc, DMA, 140°C, 20 h. ^cPd(PCy₃)₂Cl₂, DMA, NaOAc, 140°C, 20 h. ^dPd(PCy₃)₂Cl₂, DMA, DBU, 140°C, 10 h. ^ePd₂(dba)₃ (5%), P(*t*-Bu)₃ (10%), Cs₂CO₃, DMA, 140°C, 20 h. ^fPalladacycles (10%), DMA, NaOAc, 140°C, 20 h. ^gPd(PCy₃)₂Cl₂ (10%), DMA, NaOAc, 140°C, 12 h.

gave ring closed product, although it has been reported that palladacycles were effective for catalyzing aryl chloride Heck reactions.⁶ However, when bis(tricyclohexylphosphine)palladium(II) chloride [Pd(PCy₃)₂Cl₂], a catalyst known to be effective for some palladium-catalyzed carbonylation¹¹ and Suzuki reactions involving activated aryl chlorides,¹² was used, about 20% of desired product was formed when sodium acetate was used as a base. Various organic and inorganic bases were then investigated, and we were pleased to find that the strong organic base, DBU, brought about the conversion of **5d** to **1d** in ca. 90% yield. The use of tris(dibenzylideneacetone)dipalladium(0) [Pd₂(dba)₃] and P(*t*-Bu)₃ as the catalyst in DMA reduced the conversion to 50%.¹³ The introduction of the electron-withdrawing carbomethoxy group *para* to chlorine greatly enhanced the reactivity of the chloride. Again, Pd(PCy₃)₂Cl₂, which gave the desired product in good yield in 12 h, proved to be superior to either Pd(PPh₃)Cl₂ or palladacycles that gave a three component mixture after 20 h. The effectiveness of Pd(PCy₃)₂Cl₂ over Pd(PPh₃)₂Cl₂ may result from the higher electron density and greater steric bulk of the former.¹⁴ The formation of **8e** in the reaction of **5e** suggests that the palladation of the aromatic ring with either Pd(PPh₃)₂Cl₂ or palladacycles is slow allowing dechlorination to occur.

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